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A review on the oxidation stability of biodiesel

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ABSTRACT

Biodiesel consists of fatty acid monoalkyl esters and is derived from feedstocks, such as vegetable oils, used cooking oils and animal fats. Biodiesel is considered to be a promising alternative biofuel. Recently, biodiesel has received additional attention and intense research has been performed in this field all over the world due to its lower environmental impact compared to the conventional diesel fuels. The central drawback of biodiesel is its susceptible nature to oxidation due to the presence of unsaturated fatty acid portion in the ester. Oxidative degradation occurs in biodiesel on aerobic contact during storage as well as with metal contaminants. Antioxidants are very effective for the eradication of those oxidation stability problems. This article presents an overview of the factors affecting the oxidation stability of biodiesel and the methods available for the prediction of oxidation stability. The effect of antioxidants in preventing the oxidation of biodiesel is also discussed.

Contents

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1. Introduction

Currently, substitute fuels receive more attention than petroleum fuels because the source for fossil fuels is diminishing. Among the renewable fuels, biodiesel can be used for existing diesel engines without the need for much engine modifications. Biodiesel is made from locally renewable feedstock, is relatively safe and easy to handle and has a substantial eco-friendly nature compared to conventional diesel fuels because of its reduced environmental impact. The fuel properties of biodiesel are comparable with that of petroleum diesel [1–4]. In addition, biodiesel enhances fuel lubricity and improves the anti-wear properties while blending with petrodiesel. Several reports have shown that biodiesel harvests more than three times the energy required to produce it and that biodiesel has a net negative carbon dioxide balance [5–11].

Biodiesel is mainly esters, which are produced by the transesterification of vegetable oils or animal fat triglycerides with simple alcohols, such as methanol, ethanol, etc. Biodiesel can be produced from various feedstocks, such as vegetable oils (edible or non-edible), animal fats, used cooking oil, etc. The triglycerides, such as oils or fats, cannot be used directly as fuel in the existing engines due to the high viscosity of these substances. The transesterification process reduces the viscosity of the oil for use as a fuel [12,13]. Although biodiesel is prominent for petroleum-based diesel in many aspects, it has some drawbacks. The main drawback of biodiesel is the high cost of the feedstock due to its limited availability. However, the cost issue could be managed by the use of abundant sources in selected regions, such as palm oil in Indonesia and Malaysia, coconut oil in the Philippines, soybean oil in the United States, rapeseed (canola) oil in Europe, used cooking oils in highly populated areas, non-edible oils including jatropha and castor in countries with copious barren lands, etc. [14]. The use of government subsidies is another attractive feature related to the management of cost [15]. Another drawback of biodiesel is its low stability because it is more susceptible to oxidation and/or auto-oxidation during long-term storage [16]. Intense research is on-going to improve the yield, quality and stability of biodiesel as well as to reduce its production cost. Various aspects of biodiesel stability have already been investigated [1,2,16–18]. In this review, a brief outlook has been investigated for the different fuel parameters affecting/indicating the extent of oxidation stability, useful methods for stability prediction and the effect of antioxidants on biodiesel stability. The role of metal contaminants and biodiesel storage containers on oxidation is briefly examined. The exhaust gas analysis of antioxidant stabilized biodiesel fuelled diesel engine is also discussed concisely.

2. Biodiesel production

The transesterification of triglyceride lipids over lower alcohols produces biodiesel. The triglycerides are transformed into linear chain fatty acid esters by the sequential conversion of triglycerides to di- and mono-glycerides. The transesterification process is affected by several factors employed for the production of biodiesel, such as the molar ratio of glycerides to alcohol, the reaction temperature, time and catalysts, as well as the free fatty acid (FFA) and water contents in the feedstock. The process can mainly be performed with acid catalysis, base catalysis and enzyme catalysis. The reaction process under the supercritical conditions of methanol can be performed without the aid of any catalysts. Among the aforementioned methods, acid and base catalysis has received more attention, but the acid-catalysed reaction is time consuming and is not preferred in industrial-scale operations. Currently, base-catalysed transesterification is recognised as the most effective way to synthesis biodiesel because this method yields the maximum amount of biodiesel with the smallest reaction time and with fewer side products [19–21]. Base catalysis involves both homogeneous catalysts, such as NaOH, KOH, $NaOCH_3$, etc., or heterogeneous catalysts, such as MgO, CaO, Na or K, which are immobilised on different support materials including, metal oxides, etc. Among the base catalysts, heterogeneous catalysts have the additional benefit of easy separation, reusability, no soap formation, etc. [22]. Many recent reviews are available for heterogeneous catalysed biodiesel production [23–27].

The most common feedstocks for biodiesel production are vegetable oils, animal fats and used cooking oil. Edible oils, such as sunflower oil, palm oil, soybean oil, etc., have good biodiesel yield by the transesterification process. However, these crops require land use for biodiesel production that has to compete with the use of land for food production [28,29]. In addition, the price of these edible vegetable oils is higher compared to the price of diesel fuel. Thus, the use of non-edible crops, such as jatropha and castor, which can grow in barren lands, as well as used cooking oil as the feedstock, is highly recommended because these crops significantly reduce the cost of biodiesel production. Recently, many research studies are available for biodiesel production using waste cooking oil and non-edible crops [30–34].

3. Oxidation stability and fatty acid composition of biodiesel

Stability is one of the important criteria concerning fuel properties. The stability of biodiesel is lower than common diesel fuel. The formation of deposits and gum and the darkening of fuels as a result of the formation of contaminants, such as alcohols,

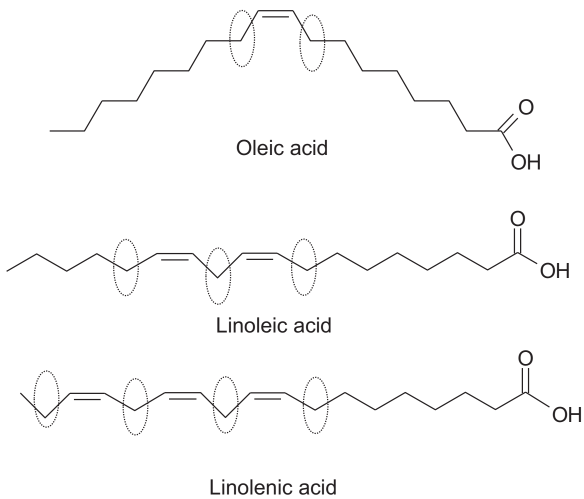


Fig. 1. Common fatty acid methyl ester biodiesel molecules.

acids, aldehydes, peroxides, etc., occur during long-term storage of biodiesel fuel [35,36]. Various processes, including oxidation in aerobic conditions, hydrolysis in the presence of moisture, thermal decomposition by excess heat, contamination of impurities, etc., account for the instability of biodiesel that can change the fuel properties considerably [1,11]. Among these processes, oxidation is one of the significant stability concerns associated with biodiesel because it has a lower resistance capacity to oxidation and can easily be affected by air oxidation during long-term storage [37].

The composition of the fatty acid portion of the biodiesel ester molecule is the most important factor that affects its properties. The composition varies based on the feedstock used for biodiesel production. When compared to diesel fuel, the unsaturation in the molecule accounts for biodiesel instability. As the unsaturation in the fatty acid chain portion increases, the biodiesel becomes more unstable. Oxidation starts at the allylic positions to double bonds. Therefore, the fatty acid composition of the ester, especially the position of and the number of allylic and bis-allylic methylene moieties adjacent to the double bond, determines the rate of oxidation. In Fig. 1, the positions in the oleic acid, linoleic acid and linolenic acid (most common unsaturated acids present in the oils or fats and thus in the biodiesel) that are vulnerable to oxidation are highlighted by a circle with dotted lines. The allylic and bis-allylic methylene moieties are the most susceptible to oxidation as a result of the radical chain reaction [38].

The oxidative stability of biodiesel is mainly related to the number of bis-allylic methylene groups adjacent to the double bond when compared to the allylic methylene groups. Thus, polyunsaturated methyl esters are more susceptible to oxidation than monounsaturated esters due to the presence of additional bis-allylic methylene configurations [38]. Hence, the relative oxidation rates for the commonly observed biodiesel unsaturated esters are ordered as linolenates > linoleates > oleates [2,16,39]. As a result of the oxidation, decomposed mixtures, including acids, aldehydes, esters, ketones, peroxides and alcohols, are formed, which affect the characteristics of the biodiesel and its activity in the engine [40]. The oxidative degradation during long-term storage occurs mainly in the presence of air, heat, light and pro-oxidants [38,41,42].

Biodiesel oxidation is of two types – auto-oxidation and photo-oxidation. Auto-oxidation is a major cause of biodiesel oxidation. The auto-oxidative degradation of biodiesel is a radical chain reaction and involves initiation, propagation, and termination steps. During the initial stages of biodiesel oxidation, the methylene groups allylic and bis-allylic to the double bonds are more active and hydrogen radicals are abstracted by radical initiators [43]. The resultant radicals interact with oxygen, which results in peroxide formation for the propagation step. The peroxides propagate the chain reaction by the further abstraction of hydrogen from the methylene moieties and form carbon radicals and hydroperoxides. Next, the newly formed carbon free radicals will again combine with oxygen and continue the propagation process. This chain process continues until the termination step, which provides the formation of stable products [41,44,45]. Fig. 2 illustrates the hydroperoxide formation during the auto-oxidative degradation of linoleic acid methyl ester. The ultimate decomposition of peroxides results in the formation of aldehydes, such as hexenals [28], heptenals, propanals, 2,4-heptadienal, etc. [13,29]. Pentane has also been detected [29]. Aldehydes are prone to oxidation, and leads to the formation of a greater number of fatty acids with a decreased chain length [14,16–18,30] when compared with the FFAs already present in the biodiesel. In addition, during hydroperoxide decomposition, oxidative polymerisation of fatty acid chains can occur and can form higher molecular weight polymers. Fig. 3 shows major oxidation products of biodiesel.

Photo-oxidation is the second type of biodiesel oxidation. Biodiesel is less affected by photo-oxidation. The initiators for auto-oxidation may also be formed as a result of photo-oxidation reactions. Auto-oxidation occurs in the presence of oxygen species, whereas photo-oxidation requires the presence of light and oxygen. Photo-oxidation is comparatively fast and proceeds with the same rate with monoenes and polyenes [46,47]. During photo-oxidation, the UV light decomposes the oxygen-containing compounds in biodiesel, such as peroxides, hydroperoxides, carbonyls, etc., and generates radicals that initiate auto-oxidation [48,49]. Photo-oxidation proceeds via two routes. One route is similar to auto-oxidation. For the second route, molecular oxygen is excited to its electrophilic singlet stage and undergoes the ene reaction with olefins, which results in the formation of hydroperoxides. Fig. 4 displays the ene reaction during the photo-oxidation of oleic acid methyl ester.

Temperature has a marked effect on the oxidation stability of biodiesel [36,50,51]. At high temperatures, highly stable conjugated structures are formed by the isomerisation of methylene-interrupted polyunsaturated olefin units. For the isomerisation process, one of the conjugated diene groups in the chain can react with the olefinic group from the nearby fatty acid chain and can form a substituted cyclohexene ring from the Diels alder reaction [50,51]. At high temperatures of 180 °C, thermal dimerisation occurs for the fatty acid methyl ester due to the Diels Alder reaction and forms the dimer. Fig. 5 shows the cyclohexene ring formed from linoleic acid methyl ester and illustrates the formation of dimers via the Diesel Alder reaction of linoleic acid methyl esters. The same reactions can also occur during the frying process of oil or fat and can adversely affect the performance of biodiesel obtained from used cooking oil or animal fat.

The fatty acid compositions (mass%) of several biodiesel feedstocks are given in Table 1[52–56]. Among the different feedstock shown in Table 1, coconut oil has a small amount of unsaturated fatty acid (9%) and may be less susceptible to oxidation. Additionally, feedstock with more unsaturated fatty acid part may have more bis-allylic hydrogen and may generate less stable biodiesel. Among the different feedstock given in the table, linseed oil (with 53% linolenic acid) may have the highest tendency for oxidation based on its fatty acid composition. Most of the parameters affecting the oxidation stability also depend on the fatty acid composition of the ester.

4. Characteristic fuel properties of biodiesel

The biodiesel obtained from different oil sources has different physico-chemical characteristics and chemical compositions.

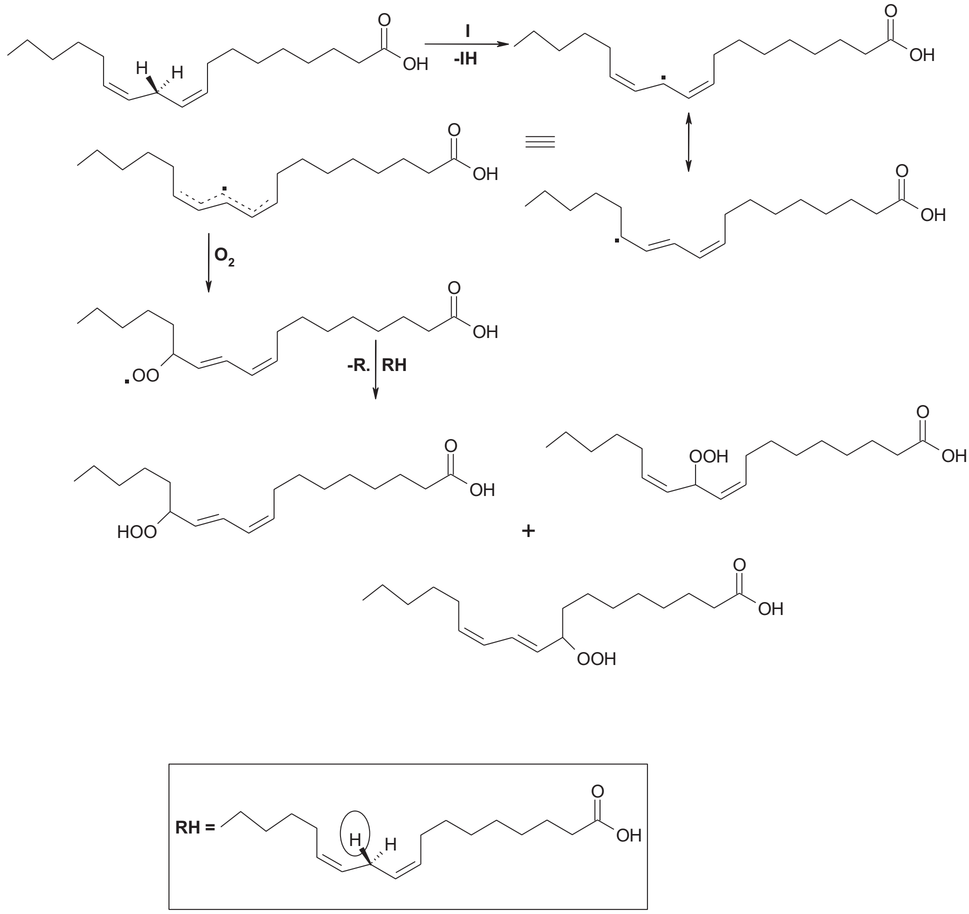


Fig. 2. Mechanism for the auto-oxidation of linoleic acid methyl ester leading to the formation of its hydroperoxides.

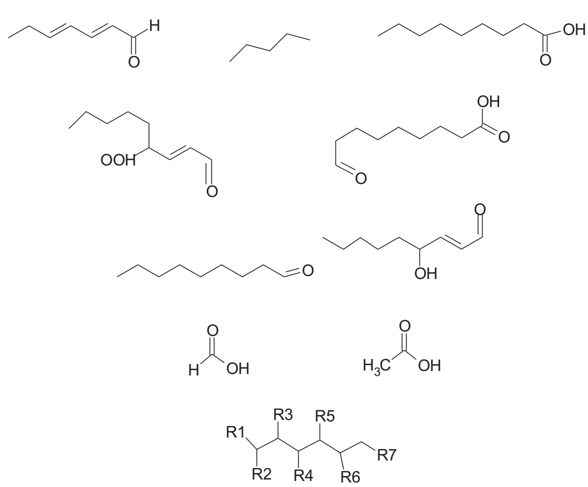


Fig. 3. Different oxidation products of biodiesel.

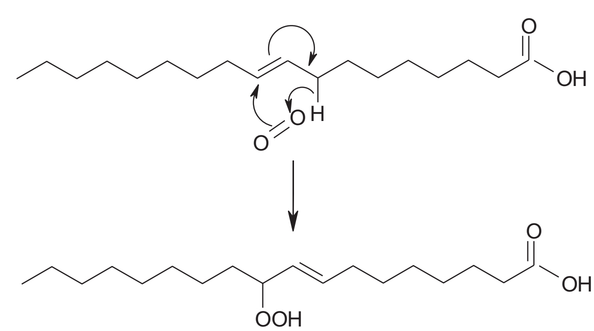


Fig. 4. Ene reaction during the photo-oxidation of linoleic acid.

The physiochemical parameters include the cetane index, calorific value, cloud point, flash point, viscosity, distillation, etc. The fatty acid methyl ester content, fatty acid composition of the ester, free glycerine and total glycerine contents, iodine index, mono-, di-and triacylglycerides, water content, methanol content, free fatty acid content, etc., are the chemical composition parameters [57]. The oxidation of biodiesel alters its chemical properties, such as the cetane number, kinematic viscosity, peroxide value, acid value, specific gravity, cloud point and pour point [58]. In addition, extensive oxidative degradation of biodiesel may produce insoluble high molecular weight polymers, which have a detrimental effect while in use. The insoluble sediments formed block the fuel lines and the filter of the engines, and an incomplete combustion and injector coking will result [59]. Therefore, the various parameters affecting the fuel properties of the biodiesel should be considered [60] because each of the parameters may directly influence the fuel properties [1]. Hence, standard specifications for biodiesel were established and are also being developed in each country so that the engine manufacturers and biodiesel producers use similar standards. The slight differences in the standards for different regions are due to the climate-related requirements for biodiesel in different countries. All modern diesel engines are compatible for the use of biodiesel as long as the fuel meets the standard specifications. The most established standards for biodiesel are the European standard EN 14214 and the American standard ASTM D6751. The standard

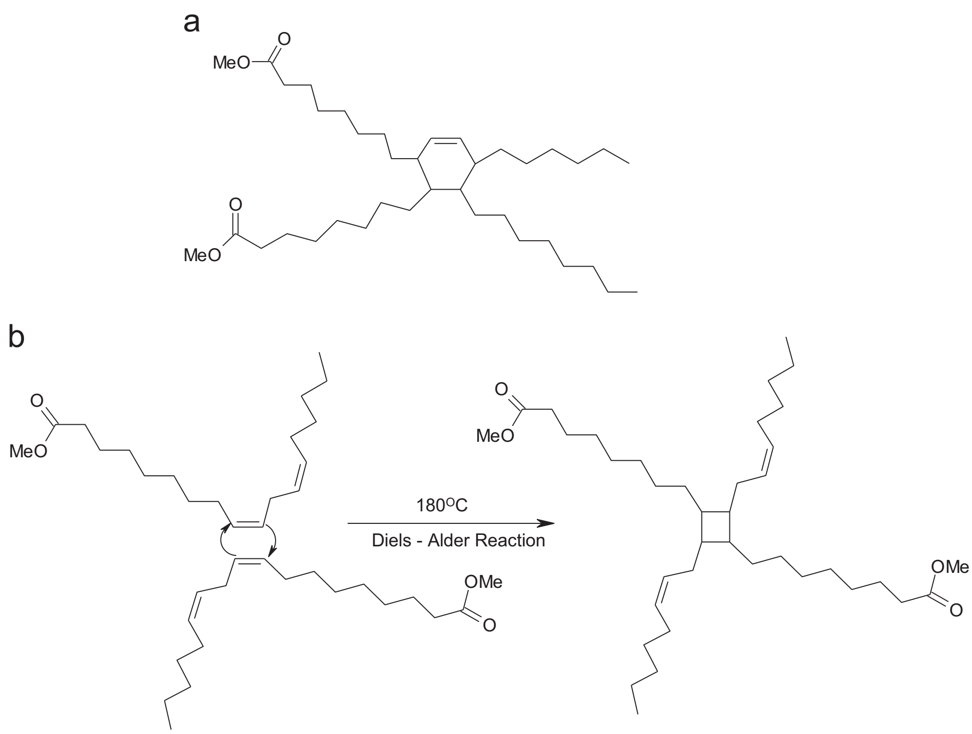


Fig. 5. (a) Cyclohexene derivative formed by the Diels Alder reaction of linoleic acid. (b) Diels Alder reaction of linoleic acid to form the dimer.

values for the fuel parameters of biodiesel (ASTM D6751) as well as comparison with some of the values of diesel fuel (ASTM D975) are provided in Table 2 [61–65]. As per ASTM D6751, the fuel must have a minimum of 3 h of oxidative stability at 110 °C [66], and thus it is an important fuel quality parameter. Because linolenic acid methyl ester contains two bis-allylic groups, it is more susceptible to oxidation. Thus, the European biodiesel standard (EN 14214) has a separate specification for linolenic methyl ester content.

5. Parameters indicating the extent of oxidation stability of biodiesel

An understanding of selected fuel parameters is highly important in evaluating the oxidation stability of biodiesel. Most of those parameters are directly related to the fatty acid composition of the biodiesel ester molecules. The important parameters that help to predict the oxidation stability of a biodiesel sample, their determination and its effect on the oxidation of biodiesel are discussed below.

5.1. Iodine value (IV)

The estimation of the IV for biodiesel fuel, which is the measure of the total degree of unsaturation, provides useful guidance for preventing various problems in engines. The IV is based on the reactivity of alkyl double bonds, and an increased IV of biodiesel indicates the possibility for the formation of various degradation products that can negatively affect engine operability and reduces the quality of lubrication [38,67]. The IV is expressed as the gram of iodine consumed per 100 g of the substance, which is the most parameter employed for determining the magnitude of unsaturation in the esters of fatty acids, fats, oils and their derivatives [43,68,69]. The local and international standard organisations provided procedures for the determination of IV in biodiesel [70–74].

EN 14111 is the European standard method available for the determination of the IV of biodiesel. The analysis is based on the Wijs method. In brief, acetic acid/cyclohexane (1:1) solvent was added to a previously weighed biodiesel sample, and the Wijs solution was added and stirred. After the addition of 20% potassium iodide, titration was conducted with 0.1 mol/L $Na_2S_2O_3$. Back titration is performed to determine the IV [75]. Several reports explain how to determine the degree of unsaturation and the IV in vegetable oils or biodiesel products using ^{1}H NMR [76–79]. M. Oromí-Farrús et al. proposed a fast and accurate method to determine the IV using ^{1}H NMR with 1,4-dioxane as an internal standard, especially when biodiesel is blended with other compounds [80]. The use of an internal standard allows the direct determination of the IV of biodiesel samples and correlates well with the volumetric reference method.

The IV indicates the tendency of biodiesel to oxidise or polymerise, which leads to the formation of insoluble sediments. An increase in the degree of unsaturation causes an increase in the iodine used. The IV considers that the nature, position in the chain and the amount of olefinic carbons in the fatty compounds are equal and thus equally reactive, which makes the IV not able to distinguish the structural differences that are present in different fatty compounds [38]. Therefore, the IV does not provide a measure to determine whether the hydrogens are allylic or bis-allylic to the double bonds, which is an important factor for determining the oxidisability of biodiesel. Biodiesel stability is not related to the total number of double bonds expressed by the IV but is mainly related to the number and position of the bis-allylic methylene moieties adjacent to the double bond [81].

The biodiesel sample supplier industry established a range for the IV from 67.1 to 133.7, which corresponds to biodiesel that originated from vegetable oils, such as soybean, canola, rapeseed, jatropha and animal fats, including chicken fat and so on [82,83]. The iodine number of FAME prepared from sunflower oil is high because of the very high content of linoleic methyl ester (C18:2) [81,84]. As per the ASTM D6751 standard, no limit exists for the IV. In some European standards, a maximum value for the IV has been

Table 1
The fatty acid compositions (mass%) of some biodiesel feedstocks.

Fatty acid	Short-hand	Coconut	Palm	Palm kernal	Sunflower	Jatropha	Castor	Soybean	Safflower	Sesame	Ground nut	Olive	Grape seed	Linseed	Chicken fat	Beef fat
Caprylic	8:0	7.0														
Capric	10:0	5.4		1.2												
Lauric	12:0	48.9	0.2	51.6												
Myristic	14:0	20.2	1.1	22.9		0.1									1.0	3.0
Palmitic	16:0	8.4	42.6	12.2	6.3	14.2	1.0	11.6	7.0	8.5	10.0	13.0	7.0	6.6	22.0	27.0
Stearic	18:0	2.5	3.8	1.3	3.0	7.0	1.0	4.0	3.0	5.4		3.7	4.0	4.4	6.0	7.0
Oleic	18:1	6.2	41.9	10.8	43.7	44.7	3.0	18.8	14.0	38.8	46.8	39.1	15.8	18.5	37.0	48.0
Rinsolenic	18:1						89.5									
Linoleic	18:2	1.4	10.4		47.0	32.8	4.2	56.1	75.0	46.3	33.4	35.4	69.6	17.3	20.0	2.0
Linolenic	18:3					0.2	0.3	8.5						53.2	1	
Arachidic	20:0					0.2				1.0		1.9				
Heneicosanoic	21:0															
Beheric	22:0					0.2						4.4				
Lignoceric	24:0											1.4				
Others						0.6	1.0	1.0	1.0			1.1	3.6		13.0	13.0

Table 2
The standard values of some of the fuel parameters of biodiesel as per ASTM D6751/EN 14214 and the comparison with the data of diesel ASTM D975.

Property	Biodiesel test method	Units	Biodiesel EN14214/ASTM D 6751	Diesel ASTM D975
Fatty acid methyl ester (FAME) content	EN14103	% m/m	96.5 min	–
Mono-glyerides		% m/m	0.80	–
Di-glycerides	EN 14105	% m/m	0.20	–
Tri-glycerides		% m/m	0.20	–
Linolenic acid methyl ester	EN14103	% m/m	12	–
Free glycerine	D6584	% m/m	0.020	–
Total glycerine	D6584	% m/m	0.240	–
Phosphorus content	D4951	% m/m	0.001 max	0.08 max
Metal I (Na+K)		ppm	5 max	–
Metal II (Ca+Mg)	EN14538	ppm	5 max	–
Flash point	D93	°C	93.0 min	60–80
Water and sediment	D2709	vol%	0.050 max	0.05 max
Kinematic viscosity, 40 °C	D445	mm^2/s	1.9–6.0	1.3–4.1
Sulfated ash	D874	% m/m	0.020 max	–
Sulphur	EN ISO 20884	mg/kg	10 max	50 max
Copper strip corrosion	D130	3	3	No
Cetane number	D613	–	47 min	40–55
Cloud point	D2500	°C	−3 to 12	−15 to 5
Carbon residue	D4530	% m/m	0.050 max	0.15
Acid number	D664	mg KOH/g	0.50 max	–
Distillation temperature (T90)	D1160	°C	360 max	338 max
Oxidation stability	EN15751	hours	3 min	–
Cold soak filterability	D7501	seconds	360 max[c]	–
Methanol content	EN14110	vol%	0.2 max	–
Lower heating value		Btu/gal	~118,170	~129,050
Total contamination	ASTM D5452	mg/kg	24 (max)	–
Organic matter (10%)	EN ISO 10370	% m/m	0.3 max	–
Specific gravity @ 60 °C	EN ISO 12185	kg/l	0.88	0.85
Iodine value	EN14111	mg I/100 g	120 max	–
Pour point	ISO 3016	°C	−15 to 10	−35 to −15

min represents minimum and max represents maximum throughout the table.

included and that would exclude the use of pure biodiesel (B100) derived from several important vegetable oils, including soybean oil and sunflower oil as clear from the IV data shown in Table 3 [85–89]. EN 14214 limited the IV to 120, and EN 14213 limited the IV to 130. However, because the oxidation mainly depends on the position of the double bond more than its number, a high IV may not be the ultimate factor for determining biodiesel stability. According to the South African standard, the maximum IV is specified as 140, which would allow the use of sunflower and soybean oils as biodiesel feedstock [90]. Vegetable oil or animal fat and their corresponding methyl esters have nearly identical IVs. However, a decrease in the IV is reported when higher alcohols were used in biodiesel production [81].

Pantoja et al. calculated the IV of the cupuaçu fat (44.3 g of I_2/100 g), açaí (61.8 g of I_2/100 g), passion fruit (133.8 g of I_2/100 g) and linseed oils (180.1 g of I_2/100 g) [91]. The iodine index of linseed oil was the highest because it is mainly composed of unsaturated fatty acids, such as linolenic acid (C18:3) as already mentioned. The cupuaçu fat had the lowest iodine index because it is rich in saturated fatty acids [91]. The mixing of biodiesel from different feedstock of varying IV will permit the use of biodiesel with a high IV. The presence of additives cannot improve the iodine number. Thus, the use of blended biodiesel with biodiesel containing more saturated fatty acids that have a low IV is favourable. The blending of these biodiesels results in an increase in the cold filter plugging point (CFPP) of the blend [92]. The production of mixtures of *C. sativa* oil methyl esters with esters of other types of oil or fat with low IVs is necessary for use as a biofuel because of the high IV of *C. sativa* oil methyl esters [93]. The mixtures containing 68% spring *C. sativa* oil and 32% (vol.)

Table 3
The IV for different oils used for biodiesel production.

Fat/oil	Iodine value (mg KOH/g oil)
Grape seed oil	124–143
Palm oil	44–51
Olive oil	80–88
Coconut oil	7–10
Palm kernel oil	16–19
Cocoa butter	35–40
Jojoba oil	~80
Cottonseed oil	100–117
Corn oil	109–133
Wheat germ oil	115–134
Sunflower oil	125–144
Linseed oil	136–178
Soybean oil	120–136
Peanut oil	84–105
Ricebran oil	99–1
Margarine “light”	37.3
Margarine	86.1
Lard	57.6
Rape oil	11.4
Crude fish oil	108.5
Tung oil	163.1
Beef fat (tallow)	46.9
Canola oil	188–193

pork lard methyl esters meet the requirements of standard EN 14214.

Usta et al. examined the different properties of biodiesel produced from tobacco seed oil [92]. Their results showed that the IV of the tobacco seed oil methyl ester (TSOME) was not within the limits of the EN 14214 standard, and an improvement in the IV was observed by blending the biodiesel produced from tobacco seed oil with a biodiesel that contains more saturated fatty acids. Usta et al. used 30 wt% biodiesel produced from waste mixed cooking oil (WMCOME) with an IV of 60 g I_2/100 g and 70 wt% TSOME to prepare blended biodiesel. The IV of the prepared blend was just below 120 g I_2/100 g. The addition of WMCOME decreased the iodine number of the TSOME below the maximum limit of the standard and improved the oxidation stability of the blend but resulted in an increase in CFPP [92].

Bouaid et al. [38] investigated the influence of aging/storage of biodiesel on the IV with samples that were prepared from vegetable oils and waste cooking oil. According to their evaluation, a change in the IV in a time period of 30 months was observed, whether it was exposed or not exposed to daylight. The observed change was a decline in the IV, which may have caused a decrease in unsaturation during oxidation. Many studies have shown a strong positive correlation between the IV of the fuel and NO_x formation [94–96] because the presence of double bonds in a chemical structure has a greater tendency to promote radical formation than single bonds. The presence of an increased concentration of free radicals leads to the formation of more NO_x [97].

5.2. Induction period (IP)

As mentioned, biodiesel oxidation is mainly the result of a radical chain reaction that causes the formation of hydroperoxides. During the initial period of storage, the formation of hydroperoxides is very low. This dead time will vary based on the nature of the FAME, the presence of additives, the conditions of storage, etc. This characteristic time period is called the induction period (IP). Any biodiesel sample is nearly stable until its IP, and thus, many of the determination methods for biodiesel oxidation stability rely on the measurement of its IP (so the measurement of the IP is mentioned under those headings) under various experimental conditions. Hence, the IP is the most important parameter in relation to biodiesel stability. Once the induction period is reached, the level of hydroperoxide, ROOH increases rapidly and results in a fast overall oxidation process [51]. The relative oxidation rate study of the methyl esters confirmed that biodiesel with more poly-unsaturations in the sample can easily experience oxidation [98]. The oxidation rate of oleic (18:1), linoleic (18:2), and linolenic (18:3) acids is noted as 1:12:25 [98]. Additionally, the stability predicting parameter, called the oxidation stability index, is related to the IP. The minimum IP limits, which are specified by the American (ASTM D6751-11b) [99] and European (EN 14214) [100] standards for biodiesel in the resistance of oxidation, are 3 h and 6 h, respectively. The Indian specification IS-15607 recommends a minimum of 6 h as the induction time [101].

5.3. Peroxide value (PV)

The PV is generally based on the primary oxidation products, such as the hydroperoxides of the biodiesel, and is a measure of the peroxide units formed during the oxidation process. The PV is measured in milli-equivalents of peroxide units per kg of the biodiesel sample. The PV influences various parameters in the fuel standard, such as the cetane number (CN), density, viscosity, etc. [102]. The increase in PV increases CN, which may reduce the ignition delay time [102,103]. The increase in PV as well as the acidity after the IP can also cause the corrosion of the fuel system components, the hardening of the rubber components, the fusion of the moving components and engine operation problems [104,105].

Several studies exist for storage stability tests for biodiesel, which show that oxidation can affect fuel quality with respect to the PV [38,106–108]. Bouaid et al. [38] report that a low PV is required for the high stability of biodiesel against oxidation. Das et al. [108] have analysed the PV of karanja oil methyl ester (KOME). According to the results obtained from the 180-day storage study, the PV increased as the storage time of biodiesel increased. Therefore, oxidation stability decreases with an increase in storage time. The experimental results show that the samples stored under “open to air inside the room” (27.76 mg/kg) and “exposed to metal and air” (27.92 mg/kg) had a high PV compared to other conditions and, hence, were more susceptible to oxidative degradation. During the biodiesel oxidation, the acid value (AV) and viscosity increased continuously at the point in which PV attained a plateau of approximately 350 mEq/kg fatty acid ester. Monyem et al. have reported steady increases in the AV and viscosity of soybean oil fatty acid methyl esters (SMEs) when they are subjected to a simulated in-use diesel engine condition, whereas PV first increased and then levelled off at a maximum value near 350–400 mEq/kg oil [109]. Dunn reported a decrease in the PV of SMEs with an increase in reaction temperature under severe thermal-oxidative reaction conditions [59]. The PV of the tested fuels (mixtures of methyl esters with fossil diesel fuel) was determined using the standard method 3960:2009. The results showed that the primary oxidation occurred intensively during the storage of biofuels and was associated with the formation of free fatty acids and an intensive and steady increase in the PV of the fuel. The intensive secondary oxidation process resulted in the formation of resins, which is characterised by the stabilisation of the PV and has not been observed in their study [107].

Pantoja et al. [91] have examined the PV of different fats and vegetable oils by the AOCS Cd 8-53 method. According to their observation, the cupuaçu fat had a low PV (3.87 mEq O_2/kg), as did the passion fruit (8.0 mEq O_2/kg) and linseed (10.0 mEq O_2/kg) oils. The high PV of açaí oil (177.14 mEq O_2/kg) indicated its

advanced state of oxidation. Xin et al. [110] have evaluated the oxidation stability of biodiesel prepared by the supercritical methanol method, which exposes biodiesels to supercritical methanol at 270 °C/17 MPa for 30 min. They have reported that supercritical methanol exposure can reduce the PV by the efficient decomposition of hydroperoxide, and they clarified that the supercritical methanol method is superior to the alkali-catalysed method for biodiesel production from oils/fats that have a high PV. From their results, the oxidation stability improved for biodiesel with a high initial PV upon exposure to supercritical methanol, whereas the stability was slightly decreased for the biodiesel sample with a low initial PV. This observation was not observed for the unexposed biodiesel prepared by the alkali-catalysed method.

Though the PV is not specified in the current biodiesel fuel standards, in the discussions above, it is an important parameter for determining the degree of oxidation and the quality of the oil because it is directly related to oxidation stability, and the primary biodiesel oxidation products include various peroxides and hydroperoxides. The initial PV is important for any biodiesel samples because it indicates the tendency for the sample's oxidation. The PV is not a suitable measure for monitoring biodiesel oxidation because it tends to increase and then decrease upon further oxidation, due to the formation of secondary oxidation products from hydroperoxides [1,109,111]. In addition, the rapid decomposition of the peroxides also limits the scope of the PV for the stability determination.

5.4. Viscosity

Because viscosity is the measure of resistance to flow, it is important due to its effect on the fuel injection system at low temperatures. Lower atomisation characteristics in the fuel injector are the result of higher viscosity and create many severe effects on engine performance [112]. The blending of biodiesel is an effective method for improving the flow properties at low temperatures [113]. Because the vaporisation and atomisation of the fuel is reduced as a result of the high viscosity of the fuel, the fuel requires additional time to mix with the air. The viscosity of biodiesel increases with an increase in the carbon chain length, the degree of saturation of the fatty acid and its ester and the presence of free fatty acids. The viscosity of the biodiesel obtained from the used cooking oil is higher than the biodiesel obtained from neat vegetable oils. Samples with cis double bond configurations have lower viscosity, whereas samples with trans double bonds have higher viscosity. However, the position of the double bond has a minor effect on the viscosity [114]. Highly viscous samples also have a high tendency for oxidation. The main reason for the rapid oxidation processes with a high viscosity is due to the isomerisation of the double bond, usually cis to trans, along with the formation of high molecular weight products. Viscosity is useful for the measurement of the oxidation progression of biodiesel. The polymeric secondary oxidation products of biodiesel cause the formation of soluble gums and insoluble sediments and will result in an increase in the viscosity.

Shahabuddin et al. [115] investigated the biodiesel oxidation stability by evaluating different properties including viscosity. The biodiesel samples were palm oil methyl ester (PME), jatropha oil methyl ester (JME), coconut oil methyl ester (COME), 20% blends of PME with diesel fuel and 20% blends of JME with diesel fuel. For all samples, the viscosity at 40 °C increased as the storage time increased. The viscosity of the PME increased to a maximum, from 4.92 to 5.97 cSt, after a storage time of 3 months. In the case of JME, the increase was from 4.81 cSt to 5.75 cSt. Diesel blended fuels had little effect on the viscosity during storage. In the case of pure diesel, the change in viscosity was minimal, and oxidation had the least affect, i.e., from 3.20 cSt to 3.69 cSt. In this study, the viscosity of COME was minimal when compared with other biodiesel samples due to the shorter chain length (C8–C14) of fatty acid part.

5.5. Structure indices

The structure indices are one of the analytical indices related to fats and oils. For lipids, the structure indices include the IV, the saponification value and the hydroxyl value [81]. The saponification value indicates the average molecular weight of a fat or oil and hydroxyl value is applicable to fatty compounds (or their mixtures) containing hydroxy groups. Most of the existing methods for the prediction of the stability of fatty acids and their derivatives are based on structural information and mainly rely on the number of double bonds. However, the allylic and bis-allylic positions on the molecule are more sensitive to oxidation than the double bond. Thus, new structural indices have been developed, such as the allylic position equivalent (APE) and the bis-allylic position equivalent (BAPE) [81]. These structural indices are the theoretical measurements for the oxidative stability determinations of biodiesel and have provided useful results.

APE is the measure of the number of singly allylic carbons present in the fatty oil or ester because a methylene group interruption exists in all poly-olefinic unsaturation. BAPE is the theoretical measure of the number of doubly allylic (bis-allylic) carbons present in the fatty oil or ester. These measurements are based on the relative rates of oxidation of these more reactive positions for unsaturated fatty acids as well as their amounts [81].

According to Jain and Sharma [2], both the APE and BAPE values are well correlated with the IP. Due to the higher oxidation rate of the bis-allylic CH_2 positions, the BAPE value is more significant for the oxidation of unsaturated fatty compounds and is the decisive index compared to the APE [90]. The linoleic acid, which has one bis-allylic position at C-11, and the linolenic acid, which has two bis-allylic positions at C-11 and C-14, are more prone to auto-oxidation than the oleates with allylic positions only. Frankel, [48] has provided the relative oxidation rates of oleates, linoleates and linolenates as 1, 41 and 98, respectively. Bouaid et al. [38] reported the use of the APE and BAPE indices instead of the IV for oxidative stability measurement because the oxidation may be more strongly influenced by the presence of small amounts of more highly unsaturated fatty compounds than by increasing amounts of double bonds in the sample. Thus, the APE and BAPE have been considered as better alternatives to the IV and are more suitable.

The APE value of different fatty compounds can be determined by [41,81]

$$APE = (ap_a \times A_{Ca}) + (ap_b \times A_{Cb}) + (ap_c \times A_{Cc} + \cdots \quad (1)$$

where A_{Cx} is the amount of each fatty compound present in the sample in percentage, and ap_x is the number of allylic positions in a specific fatty acid compound. The same equation is valid for the determination of BAPE, but we have to consider the number of bis-allylic positions rather than the number of allylic position in a fatty compound.

Each of the oleic acid (C18:1), linoleic acid (C18:2) and linolenic acid (C18:3) unsaturated fatty acid chains has two allylic positions. Thus, the APE of a mixture containing those fatty acids can be determined by

$$APE = 2 \times (A_{C18:1} + A_{C18:2} + A_{C18:3}) \quad (2)$$

The BAPE of such a mixture can be calculated by

$$BAPE = A_{C18:2} + 2 \times A_{C18:3} \quad (3)$$

because the oleic acid does not have a bis-allylic position, and the linoleic acid and linolenic acid have one and two bis-allylic

positions, respectively. The average number of allylic or bis-allylic positions per molecule in a mixture of fatty compounds can be obtained by dividing the APE and BAPE indices by a factor of 100 [81].

5.6. Oxidisability (OX)

Another stability index used for the investigation of biodiesel stability is the oxidisability, which is a dependent variable that measures the relative rate of oxidation [116]. Neff et al. [116] expressed the OX with

$$OX = [0.02(\%O) + (\%L) + 2(\%Ln)]/100 \quad (4)$$

where O, L, and Ln refer to the amount of oleic acid (18:1), linoleic acid (18:2) and linolenic acid (18:3) present in the test sample. The coefficients specified for oleic, linoleic, and linolenic fatty esters represent the relative rates of oxidation of these compounds [98]. The OX applies only to the biodiesel that predominantly contains 18 carbon fatty acid units that originated from lipids, such as soy, tallow, etc. [117]. The increase in insoluble formation and the reduction in induction time is highly influenced by the oxidisability.

5.7. Oil stability index (OSI)

The oil stability index (OSI) is an important parameter that measures the relative oxidative stability of fatty acid-based materials. The measurement is performed isothermally but at elevated temperatures to accelerate oxidation. The OSI determination is an approved method by the American Oil Chemists Society (AOCS) for the measure of the relative resistance of fat or oil to oxidation. The OSI is more reliable than the Active Oxygen Method (AOM), but for quickly oxidisable samples, (OSI times <3 h), the method's precision is low when compared to stable samples. The OSI was calculated using the conductivity measurements of water contaminated with the volatile organic compounds that evolved as a result of oxidation of the oil, fat or its derivative, such as biodiesel. Additionally, the Rancimat method of stability determination is related to the OSI measurements.

Typically, the OSI time is measured as follows [118]. A known amount of sample is weighed in a glass test tube and is placed in a heating block at a temperature of 110 °C. Next, clean, dry air is bubbled through the sample to promote oxidation. Then, the effluent stream of air is bubbled through a collection port filled with ultra-pure water. Next, an electrode is placed in the water to monitor the conductivity. As the sample oxidises, volatile organics are given off, become trapped in the water and increase the conductivity. Based on the plot of conductivity versus time, the inflection point is noted and is defined as the OSI time.

5.8. Acid value (AV)

Another parameter used to understand biodiesel degradation is the acid value (AV) because it is directly related to stability. The acid number is a measure of the amount of carboxylic acid groups in a chemical compound and can be used to quantify the amount of acid present. The AV is the quantity of base, expressed in milligrams of potassium hydroxide that is required to neutralise the acidic constituents in one gram of the sample.

Formally, the AV was not used for the evaluation of oxidative stability but is useful for assessing the quality of stored biodiesel and is included in the standards [90]. The biodiesel ester molecule has a tendency to hydrolyse to alcohol and acid in the presence of air or oxygen. The presence of acid will lead to an increase in the total acid number [119]. Thus, the presence of water in biodiesel should be minimised. The increasing peroxide formation during the oxidation of biodiesel will eventually increase the AV as the peroxides experience complex reactions, including a split into more reactive aldehydes, which further oxidise to form acids. An increase in the oxidation causes an increase in the acid number. In addition to the oxidation and hydrolysis products, the residual mineral acids from the production process are responsible for the presence of acidic compounds in biodiesel.

The standard methods for the evaluation of the acid number for mineral oils and biodiesel include ASTM D974 and DIN 51558. Specifically, the European Standard EN 14104 and ASTM D664 for biodiesel are widely used [120]. An alcoholic solution of KOH is used in the EN 14104 method for titration, and phenolphthalein is used as an indicator. The ASTM D664 method adopts potentiometric titration for AV determination [121]. Typically, 20 g of the sample mixed with 20 mL of solvent (50 ol% of toluene + 49.5% isopropanol + 0.5% water) was titrated with a 0.01 mol L^{-1} alcoholic solution of potassium hydroxide. In the ASTM D664 standard, a silver/silver chloride glass electrode was used [122]. For the EN 14214 and ASTM D6751 standards for standard biodiesel fuel, the acid number should be lower than 0.50 mg KOH/g.

Many studies show an increase in AV during oxidation [38,106,123,124]. According to Udomsap et al., the AVs of all waste cooking oil methyl ester samples increased over time and at a faster rate for higher temperatures as a result of a higher degradation rate [125]. The effect of accelerated oxidation on soybean oil and methyl ester was investigated by Romano [126] by aerating the samples (30 L/h) at 140 °C for 100 h. He noted that the AV of the ester increased more rapidly than the soybean oil. An extensive set of oxidation tests were investigated by Canakci et al. with variables such as temperature, water, and blend level and with diesel fuel [123]. The effect of different variables such as the oxygen flow rate, extended time, etc., for the PV, AV, and viscosity of soybean oil methyl ester biodiesel was studied. The acid value steadily increased with time and with the O_2 flow rate [123].

Berrios et al. studied the degradation of several biofuels (sunflower methyl esters (SuME), used cooking oil methyl ester (UCOME) and blends with commercial diesel) under different storage conditions over a 6-month period [127]. The temperature was similar to the temperature used in commercial tanks and had small air turnover and the absence of light. The evaluation of the AV during the storage time showed an increase for all of the samples. The AV exceeded the limit (based on EN 14214) after 30, 45 and 150 days for SuME, UCOME, and B20 blend, respectively. The AV of SuME samples stored at 45 °C in glass bottles had the highest increment. The temperature showed a marked influence on the AV when compared with the presence of metal in the studied sample. The results showed that stainless steel has no influence on the AV. According to the study by Lebedevas et al., the acidity of the blend of summer and winter *C. sativa* oil and pork lard methyl esters exceeds the requirements of the standards by nearly twofold after 14 months of storage [107]. Bouaid et al. investigated the storage stability of biodiesel made from three different vegetable oils and used frying oil over a storage time of 30 months and under different storage conditions by analysing the various fuel properties for that period [38]. The specification limit of the AV was exceeded in the case of biodiesel from high erucic *Brassica carinata* oil, low erucic *Brassica carinata* oil and used frying oil, which were exposed to daylight after a storage time of 12 months. In the case of samples without light exposure, only biodiesel from low erucic *Brassica carinata* oil led to a value exceeding 0.5 mg KOH/g after a storage time of 12 months. In their study, the AVs remained constant until the 4th month and then took a significant upward trend, except for used frying oil methyl ester (UFOME), which showed an increase with time without any dead period. The results show that the AV of the fuel stored in daylight increased at a faster rate than the fuel stored in

the dark after 4 months of storage. The previous studies have shown that the AV has a good potential for monitoring biodiesel quality during storage [59] while evaluating oxidation stability. An elevated value of the acidity index is not favourable because it affects the engine's metallic parts and leads to corrosion [128].

5.9. Fatty acid methyl ester (FAME) content

A biodiesel sample is suitable for use as a perfect fuel when it meets the international standard specifications. As per the different standard specifications, the methyl ester content in biodiesel fuel must be a minimum of 96.5% [129]. Thus, this parameter is of very high significance. The conversion of oil and FAME yield may vary based on the method of preparation, the nature of the catalyst, the catalyst amount, the reaction temperature, the reactant molar ratio, etc. Different methods exist for the determination of the FAME content, such as the analysis of Gas Chromatogram, FTIR spectra, and NMR spectra, among others.

The analysis as per the ASTM D6584 standard is as follows: the weight percentage of methyl esters in the biodiesel sample is evaluated using a Gas Chromatograph equipped with a flame ionisation detector. The capillary column with an internal coating of 5% phenyl polydimethylsiloxane and cross-linked upper phase is used for the sample analysis. The carrier gas used is nitrogen. The oven temperature programme starts at 50 °C, and is heated to 180 °C at a heating rate of 15 °C/min. Then, the oven temperature is further heated to 230 °C at a rate of 7 °C/min. Finally, the temperature is increased to 380 °C at a 30 °C/min rate, and the oven remains at this temperature for 20 min. For sample preparation, 100 mg of biodiesel is first derivatised by 100 μL of MSTFA. The mixture is shaken well and allowed to remain at room temperature for 15–20 min. Approximately 8 ml of n-heptane is then added and mixed well. Then, 1 μL of the prepared sample is injected into the cool-on-column port and the analysis is started. The detector temperature is 380 °C and the injector follows the oven track. Mono-, di-, and triglycerides were determined by a comparison with monoolein, diolein, and triolein standards. The chromatogram and peak integration report are collected to analyse the FAME content [21,129].

The methyl ester content decreases on storage [130] because the unsaturated fatty acid esters are oxidised. Thus, the evaluation of methyl ester content is highly informative for analysing biodiesel oxidation. Cherng-Yuan Lin and Jung-Chi Lee [130] investigated the oxidative stability of biodiesel produced from crude fish oil and from the waste parts of marine fish by analysing various parameters, including the methyl ester content. The fish oil glyceride is rich in polyunsaturated fatty acids. The biodiesel sample stability was investigated with and without the presence of antioxidants. Among the different samples, biodiesel stored without the presence of any antioxidant-degraded maximum based on the FAME content analysis. From the study, it was concluded that a high operating temperature causes a greater degradation rate and a significant decrease in the methyl ester content.

5.10. Density

Density, the measure of the mass per unit volume (kg/m^3) is an important fuel parameter which is influenced upon biodiesel oxidation. For all biodiesel samples, the trend in the change in density is same where as it increases with storage time. This increase was the result of the presence of oxidation products. The density of samples with high saturated fatty acid ester content and small chains also becomes high since the fuels containing shorter chain hydrocarbon and more saturated fatty acid have more tendencies to get crystallised. These result in the decrease in its volume and thus increase in the density [115]. The mass of the sample also get increased as the result of the presence of oxidation products. It is also reported that the thermal instability of biodiesel is the major factor increasing the density, as it increases the rate of oxidation. The oxidation process increases the mass of oil and fat due to the formation of insoluble sediments and this again increases the density.

6. Methods used to predict the stability of biodiesel

A wide variety of techniques have been used for the stability determination of fatty acid esters. The type of test method depends mainly upon the nature of the stability, including thermal stability, oxidation stability and storage stability. For the determination of thermal stability, the Rancimat test, ASTM D6408-08 and TGA/DTA are used. For the storage stability determination, a modified Rancimat test, ASTM D4625-04, and ASTM D5304-06 are used. The Active Oxygen Method (AOM), ASTM D2274, ASTM D3241, EN 14112, and ASTM D5483 are the methods used for the oxidation stability determination of biodiesel. Jain and Sharma, Liang et al., Westbrook, Hasenhuettl and Wan, etc. [17,131–133] compared different test methods and found that the ASTM D2274 and Rancimat test are prominent. For each of the methods, the nature of the measurement, its importance, and the major inference from the analysis are outlined in the following sections.

6.1. ASTM D4625-04

The ASTM D4625-04 method is the most widely established method for the estimation of storage stability for the middle distillate petroleum fuels [134]. In this method, the fuel is stored at a temperature of 43 °C for a period of time, such as 24 weeks. The sample is then filtered to evaluate the insoluble sediments of the sample, and the remaining filtrate was investigated to determine the total AV and kinematic viscosity. These tests must be carried out weekly. For the precipitation of polar polymers present in the sample, isooctane is added. This modification is necessary in cases where soluble products are formed by the oxidation [17,132,135]. Because the temperature in the test conditions is slightly higher than room temperature, fuel oxidation and other degradative reactions lead to the formation of sediment that is mildly accelerated in this method when compared with typical storage conditions. In this method, the storage stability prediction is more reliable than the other more accelerated tests. However, because the storage periods are lengthy (4–24 weeks), the test method is not appropriate for quality control testing and only provides a tool for research on the storage properties of fuels. The storage material is also an important aspect for this study.

6.2. ASTM D6468-08 – light reflectance method

For the high temperature stability determination of the middle distillate fuels (including biodiesel), the ASTM D6468-08 method is more prominent [136]. Here, the sample is aged at 150 °C in open tubes with air contact for approximately 90 or 180 min. After the aging process, the sample is cooled and the insoluble sediments are filtered and estimated by the light reflectance method of the filter paper. For comparison purposes, a blank is conducted without the sample using an unused filter pad [17,132,135]. The filter paper used for this ASTM method has a nominal porosity of 11 μm, and thus, it cannot capture all of the sediment formed during aging, although it allows differentiation over a broad range of particle sizes for the sediments. The method of reflectance measurements can be affected by the colour of the filterable insolubles and may thus not be successfully correlated to the mass

of the material that is filtered. Thus, the accuracy of the method is not 100%. This method can provide an estimate of the stability of fuel when exposed to high temperatures in situations, including a recirculating engine or burner fuel delivery system, and under other high temperature conditions with limited exposure to air. In addition, the test method is also helpful in the study of operational problems related to fuel thermal stability. This method is not suitable for fuels whose flash point is less than 38 °C. This test method is also not suitable for fuels containing residual oil and is thus only suitable in the estimation of the high temperature stability of biodiesel with a very high FAME content.

6.3. ASTM D7462-11

This accelerated test method is the standard method for the testing of oxidation stability of pure biodiesel and blends of biodiesel with middle distillate petroleum fuel [137]. The oxidation stability is accessed by this method at specified oxidising conditions at 95 °C by the formation and measurement of insoluble degradation materials. It is a rapid method in comparison with the ASTM method D4625. Pure biodiesel, B100, composed of alkyl esters, is a good solvent for a range of chemicals including polymers and thus some products of oxidative degradation get dissolved in it. Thus, even though some B100 undergo significant degradation, it may show little or no sediment formation. The failure of this method lies there, since many petroleum diesel fuels have relatively poor solubility for products of oxidative degradation. Consequently the blends, especially with lower biodiesel content could show higher sediment levels. A paraffinic dilution procedure was also suggested by ASTM to evaluate oxidative degradation of B100 for degradation materials that are soluble in B100, but insoluble in iso-octane. The addition of iso-octane allows the precipitation and measurement of biodiesel soluble fragments.

6.4. ASTM D2274 – gravimetric analysis

This method is the standard method used for the oxidation stability determination of distillate fuel oil and also helps to measure the tendency of biodiesel to form polymers and insoluble sediments [138]. This accelerated method is based on the filtration, which is followed by the gravimetric analysis of the insoluble materials that are formed by the oxidation in the presence of heat. Here, the sample is first aged at 95 °C for 16 h by the bubbling of oxygen at a rate of 3 L/h. The insoluble sediments formed by the thermal oxidation stick on the oxidation cell and are detached with the help of a tri-solvent containing equal parts of toluene, acetone, and methanol. The solvent is then evaporated to recover the insoluble sediments (insolubles) formed. The total yield of the insolubles, expressed as milligrams per 100 ml, is reported as total insolubles. An additional analysis exists for the determination of biodiesel-soluble polymers. In this case, iso-octane is added to the sample so that the soluble polymers will precipitate. This precipitate is filtered to acquire the measure of the soluble polymers [17,132,135]. The use of an elevated temperature and a pure oxygen atmosphere for the test may cause differences in the nature and amount of insolubles formed in real storage situations. This test method is also not applicable to fuels containing residual oil. This test method has not been validated for the testing of biodiesel or blends of middle distillates and biodiesel meeting ASTM specifications. The test method D7462 is more suitable for testing B100 and all blends of middle distillates and biodiesel because samples containing biodiesel can cause a partial dissolution or compromise of the membrane filter, providing erroneous results.

6.5. Active oxygen method (AOM) – PV measurement

This is the least effective method for the oxidation stability determination of biodiesel because PV is the stability parameter measured in this test. Here the sample is heated at a programmed temperature by the continuous bubbling of air with a particular flow rate. The time required to attain a specific PV is determined [17,139]. The trend in PV varies with time since the peroxides undergo fast degradation and thus PV measurement cannot be a suitable method for monitoring the oxidation stability. Other major defects of the AOM method are that it is more labour intensive, required chlorinated solvents, and was generally not performed in a consistent manner from laboratory to laboratory.

6.6. ASTM D3241 or JFTOT method – ellipsometric method

The ASTM D3241 method is the standard test method for high temperature thermal oxidation stability of aviation gas turbine fuels and requires some additions if this method is employed for the oxidation stability determination of biodiesel [140]. This method uses the Jet Fuel Thermal Oxidation Tester (JFTOT) and exposes the test fuel to conditions that can be interrelated to those conditions occurring in gas turbine engine fuel systems. This method can be used to assess the level of deposits that form when liquid fuel contacts a heated surface that is at a specified temperature. Here, the test fuel is pumped through a heater at a fixed flow rate. As a result, degradation products are formed and accumulate on the precision stainless steel. The amount of accumulated degradation products is determined by the ellipsometric method [17,132,141]. Due to the small size of the accumulated degradation products, this method is inadequate, and additional investigations are needed to improve the applicability of this method.

6.7. EN 14112, Rancimat method – IP measurement

Initially in the Rancimat method, FAMEs of the sample are oxidised to peroxides as the primary oxidation products. The peroxides are then completely decomposed to form the secondary oxidation products. These products include volatile organic compounds and low molecular organic acids, which are mainly formic and acetic acids. The Rancimat method is also the usual and the official method for determining the oxidative stability of oils and fats by the American Oil Chemists' Society (AOCS). In this method, the temperature range is usually limited to a maximum of 130 °C [136].

In a brief experiment, the sample is first subjected to a heat treatment at a quantified temperature (110 °C). After that, air is bubbled through the sample so that the oxidation of the sample takes place. As a result of the oxidation process, a release of some gases along with the air occurs, which is then passed to deionised water in a flask. The flask has an electrode, which is connected to a device for a measurement of the conductivity. The induction period (IP) is measured for this test method. Here, the IP is noted as the time at which the conductivity starts to increase very quickly. The continuous measurement of this conductivity gives an oxidation curve. The point of inflection of this curve is known as the induction period. Volatile acidic gases, such as formic acid, acetic acid and some other acids, are produced by the oxidation and are absorbed in the water, which is the main reason for the increment in the conductivity and in the IP measurement [17,132,142]. A modified Rancimat test is also used for the determination of the storage stability of the samples [143]. Here, the oxidation is carried out by the passage of air on the surface of the sample heated at 80 °C for approximately 24 h. Afterwards, the PV and the amount of ester and polymers present in the sample

are measured. This method is also applicable to the thermal stability determination in which the sample is subjected to the same treatment at 200 °C for 6 h. The modified Rancimat method is significant due to its repeatability and simplicity.

However, the Rancimat method has serious limitations. The air flow through the sample during the analysis can carry volatile compounds that are already present in the sample to the deionised water, which may contribute to the conductance and in turn affect the IP measurement [144]. Contamination should be avoided during the analysis.

6.8. Spectrofluorimetry and multivariate calibration

Meira et al. reported a spectrofluorometric method for the determination of oxidation stability of soy biodiesel with the assistance of a multivariate calibration [145]. In this study, the oxidation stability predicted was in concurrence with the results obtained by the Rancimat EN14112 reference method. The advantage of this method is its fast performance and accurate results; the analysis required only 20 min for oxidation stability determination, and the calibration models were prepared using the Partial Least Square (PLS) analysis. When compared to other methods, spectrofluorimetry did not demand any sample pretreatment. Additionally, spectrofluorimetry is a non-destructive analytical technique that allows the reliable, direct and fast determination of several properties.

The experiment is briefly mentioned here. The excitation was initiated at 200 nm in increments of 25 nm, and the emission was obtained in the 230–800 nm range in increments of 0.5 nm. A 3D excitation–emission matrix was built with the experimental data and was transformed into a 2D general matrix. A multivariate calibration model was developed by PLS regression. For each matrix, a PLS model was built using the mean centred fluorescence spectra as independent variables and the measured induction period as the dependent variable. For the calibration step using PLS, the relationship between the spectra and the IPs was estimated from a set of reference samples. In the prediction step, the results for the calibration were used to estimate the IP from an unknown sample spectrum. In the study by Meria et al., known reference samples consisted of soy oil and soy biodiesel at different degrees of oxidation according to the time points [145]. The analytical results of the models presented a high correlation between the real and predicted values.

6.9. ASTM D5483 – pressure differential scanning calorimetric measurements

The ASTM D5483 method is mainly aimed for the measurement of oxidation induction time (OIT) of the lubricating greases based on the Pressure Differential Scanning Calorimetry (PDSC). If the test is conducted in an isothermal pathway, then the OIT is measured and in the non-isothermal procedure, the oxidation temperature (OT) is measured as the stability parameter [17,132]. This PDSC based method is useful for research and development, quality control and specification purposes. In PDSC, the OT is determined in the dynamic measurement and the OIT is obtained in the isothermal curve [44].

6.10. TGA/DTA method

Temperature has a significant role in the stability of biodiesel, especially for the oxidation stability [18]. Dunn investigated a relationship between the temperature and the oil stability index (OSI) of biodiesel and stated that with an increase in the temperature, the rate of oxidation of the sample also increases, and as a result of this increase, the OSI decreases [36]. A rise in temperature causes the parameters such as the PV, AV, and viscosity to increase due to the thermal degradation and the Diels Alder reactions [1,59]. In addition to the Rancimat and ASTM methods of evaluation of biodiesel stability, the TGA/DTA method has a prominent role in this respect. Jain and Sharma reported that the TGA/DTA is helpful for the assessment of biodiesel stability relative to the oxidation [16,18]. In the TGA measurements, the change in value of any parameter is measured with temperature at different conditions. TGA can be performed either in the presence or absence of oxygen. The TGA analysis is used for the determination of some of the properties of triglycerides and their derivates, such as thermo-oxidative behaviour and stability, specific heat, degree of unsaturation from melting and crystallisation oil profile curves, high pressure oxidation – IP measurements, etc. The onset temperatures measured from the TGA analysis provide the resistance of the sample to thermal oxidative degradation and a direct correlation between the onset temperature and the oxidisability of the sample. As the sample becomes easily oxidised, the onset temperature decreases [135]. Based on the high precision and sensitivity of the method, the TGA/DTA method is widely employed for determining the thermal stability and the thermo-oxidation behaviour of oil and biodiesel. The thermal stability is directly correlated with the chemical structure of the sample, and the samples with highly unsaturated fatty acids are less stable than the saturated molecules.

6.11. Analysis of the IR spectra

The usual methods of oxidation stability determination are slow, tedious and time consuming, as evident from the above discussions. Comparatively, IR is an easy, simple and fast technique for sample analysis.

The characteristic peaks found in the FTIR of biodiesel molecules include the strong ester peaks at 1750 cm^{-1} (the C=O vibration), the C–O vibrations of approximately 1170–1200 cm^{-1}, and a signal at 1435 cm^{-1}, which is the methyl ester group ($-O-CH_3$) with its deformation vibration [146]. In addition, peaks that indicate the double bond (3000 cm^{-1}, 725 cm^{-1}, etc.), will be prominent in the spectra [146]. Upon degradation, the bands at approximately 3000 cm^{-1} (HC=CH stretching) and 725 cm^{-1} (out-of-plane bending) will show a decrease in their intensity, indicating a decrease in unsaturation. Oxidative polymerisation accounts for this observation [146]. Furlan et al. investigated biodiesel oxidation using infrared spectroscopy [147]. In their report, the IR spectra were highly affected as a result of the degradation because hydroxyperoxides, alcohol, acids, aldehydes and ketones were formed during the oxidation. Because an additional formation of carbonyl groups occurs upon oxidation, monitoring of the band associated with the second harmonic of the carbonyl, in the region between 3500 and 3400 cm^{-1}, is helpful in evaluating biodiesel stability. The oxidation of soybean and crambe biodiesel was analysed by FTIR measurements, and more carbonyls are formed in soybean biodiesel in comparison with crambe biodiesel, which shows the less stable nature of soybean biodiesel to thermal stress [148].

Conceio et al. investigated the thermal and oxidative degradation of castor oil biodiesel [146]. The degradation was analysed from thermogravimetric and calorimetric profiles in addition to the analysis of spectroscopic data. Castor oil and the biodiesel have ricinoleic acid as the major component, contain a hydroxyl group and thus display additional IR bands at 3440, 850, and 1000 cm^{-1}. The IR spectrum of degraded samples at 210 °C indicates oxidation by displaying a decrease in the intensity of the bands at 3007 cm^{-1} and 724 cm^{-1} due to the decrease in unsaturation representing the oxidative polymerisation.

Both near and middle infrared (NIR and MIR) spectroscopy are successful in monitoring the quality and stability of biodiesel and its blends with diesel fuel [149–154]. MIR and NIR in connection with multivariate calibration are now employed in analysing the quality of pure biodiesel (B100) and in monitoring the transesterification reaction [155–161]. Multivariate NIR spectroscopy was used to evaluate biodiesel stability by analysing various fuel properties such as the IV, water content, CFPP, kinematic viscosity, methanol content, density, AV, etc. [156–158].

7. Stability of biodiesel/petrodiesel blends

The blending of biodiesel with petrodiesel could improve the oxidative stability of biodiesel because petrodiesel is more stable to oxidation than biodiesel. Thus, the stability of the blended biodiesel is different from the pure biodiesel. Biodiesel can be blended with petrodiesel at different concentrations, such as B5 (5% biodiesel), B10 (10% biodiesel), B20 (20% biodiesel), B50 (50% biodiesel), and B80 (80% biodiesel). As already mentioned, B100 is the pure biodiesel. The stability of the blend depends on both the contents and the factors affecting the stability of biodiesel and petrodiesel. The same trend of biodiesel stability will be imitated in its blend as well and will be strongly dependent on the percentage of biodiesel in the blend. The more the biodiesel content in a blend, the lower is its stability, since biodiesel is more prone to oxidation. Factors affecting the stability of petrodiesel can also be determining factors for the stability of the blend, such as the sulphur content, catalytically cracked compounds, etc. [128].

8. Effect of antioxidants on the biodiesel stability

Although biodiesel oxidation is difficult to avoid, its minimisation is a new topic of research interest. The most effective method for the prevention of biodiesel oxidation is avoiding contact with oxidising conditions as well as decreasing air contact, storing in a dark room in stable containers, keeping at low temperatures at inert conditions, etc. [11]. The above conditions are difficult to achieve, and hence, the use of chemicals is of substantial concern. To increase the oxidative stability of biodiesel, the most active and commercial method is the use of antioxidants, which are also effective for the biodiesel blends. Antioxidants have an enhanced role in the delay of oxidation by the extension of the induction period.

Chain breakers (peroxide radical quenchers) and hydro peroxide decomposers (reducing agents) are the most common antioxidants [162]. The chain breaker interacts with the peroxide radical, and an auto-oxidation reaction takes place and results in the formation of an antioxidant free radical, which easily stabilises without any further actions. The hydroperoxide decomposer antioxidant reacts with hydro peroxides and converts them to alcohols. In this case, the antioxidant is transformed to a harmless oxidised form. In addition, metal chelating agents and acid neutralisers are another category of antioxidants [162].

Vitamin E (tocopherols and tocotrienols) is a naturally occurring antioxidant that exists in α, β, γ and δ forms. Vegetable oils have a considerable amount of antioxidant content, but the levels are reduced as a result of the oil refining process [162]. The tocopherols provide a lower effectiveness compared to the synthetic antioxidants when they are added to biodiesel. Cardanol oil is another effective natural antioxidant extracted from cashew nut shell liquid [163]. Citric acid and caffeic acid (CA) are other naturally derived antioxidants that are used as biodiesel stabilisers [164,165].

The major synthetic antioxidants are butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), tertbutylated hydroquinone (TBHQ), pyrogallol, i.e., 1,2,3-trihydroxybenzene (PY), and propyl gallate, i.e., propyl 3,4,5-trihydroxybenzoate (PG) [166]. Baynoxs is the commercially available synthetic antioxidant widely used for the storage of biodiesel [167]. The use of di-tertbutylhydroquinone (DTBHQ), poly(1,2-dihydro-2,2,4-trimethylquinoline) (Orox PK), tris (nonylphenyl) phosphate (Naugard P), tert-butylated phenol derivative (TBP), octylated butylated diphenyl amine (OBPA), N,N'-diphenyl-phenylenediamine (DPPD), 2,6-di-tert-butyl-1,2-dihydroxybenzene, diphenylamine (DPA), 2,2′-methylene-bis(4-methyl-6-tertbutylphenol) (MBMTBP), Ethanox 4760E, p-phenylenediamine (PDA), gallic acid (GA), N,N′-diphenyl-p-phenylenediamine (DPD), Ethoxyquin, Ionol BF 200, etc., was also successful for improving biodiesel oxidation stability [105,168,169]. BHA, BHT, PG and vitamin E are chain breakers, whereas sulphides, phosphides, etc., are peroxide destroyers [170].

The role of each antioxidant on biodiesel varies with the feedstock, and the oxidative stability is dependent on the FAME composition [171,172]. Some techniques such as fractional crystallisation or hydrogenation, etc. were employed to reduce the unsaturated fatty acid content in the oils to increase the oxidation stability [173].

In the case of the antioxidants with phenolic groups, the activity mainly depends on the position of the phenolic groups and especially the 1,2 or 1,4 positions in the aromatic ring. Here, the hydroxyl groups present in the antioxidants facilitate the delivery of their protons, causing a decrease in the formation of radicals and their propagation and delay the oxidation rate in a considerable manner [174]. Antioxidants such as PY, TBHQ and GA were more effective due to their molecular structures compared to BHA and BHT. Most antioxidants have two hydroxyl groups, which are attached to the aromatic ring, but in the case of BHT and BHA, only one hydroxyl group is observed in the aromatic ring. Antioxidants such as TBHQ and PY provide more active sites for the development of a complex between the free radical of the sample and the antioxidant [175]. This complex is responsible for the methyl ester stabilisation. The lower antioxidant activity of BHT and BHA is also attributed to their relatively high volatility, as these additives will be lost in the initial periods of the heat treatments in the Rancimat method [175]. The storage stability with the addition of antioxidants depends mainly on the antioxidant type and concentration.

The addition of antioxidants has a positive role in the viscosity of the biodiesel samples. During the biodiesel storage period, the formation of oxidised compounds causes the viscosity to increase. However, the addition of proper concentrations of antioxidants, such as PG, BHT and BHA (1000 ppm), causes the viscosity of biodiesel to remain under the ASTM limit (1.9–6 cSt) [108]. Table 4 lists selected studies on the evaluation of biodiesel oxidation stability upon antioxidant addition [125, 176–185].

9. Effect of metal contaminants and the storage container on the stability of biodiesel

The presence of metal contaminants is another reason for the deterioration of biodiesel during storage. Eduardo Pereyra mentioned about the storage materials for biodiesel [43]. According to the report, biodiesel (B100) is not fully inactive with the metals and the plastic vessels during its long time storage. Biodiesel undergoes an interaction with the metals, especially with Cu and its alloys, and as a result, insoluble sediments are formed in bulk quantities by the oxidation process. Among the different metals, Cu has the strongest catalysing effect on the oxidation process. In addition, biodiesel is infused into plastic materials, such as

Table 4
Studies on the evaluation of biodiesel oxidation stability upon antioxidant addition.

Antioxidant used/stability order	Biodiesel methyl ester	Effect in stability	Method of stability evaluation/ specification	Remarks	Reference
PY > PG > TBHQ > BHT > BHA	*Jatropha curcas*	Thermal stability increased with increase in the amount of antioxidants.	Rancimat & TGA	A dosage of 100 ppm of PY is the minimum concentration required to meet EN 14112 specification	[176]
PY > PG > BHT	Croton oil	Increase in dosage of antioxidants increased the oxidation stability	EN 14214	IP 7.59 h, 12.13 h & 6 h for PY, PG & BHT respectively Optimum antioxidant concentration differ with antioxidant	[177]
TBHQ	Cotton seed oil	Oxidative stability increases linearly with the amount of antioxidant	EN 14112	Addition of 300 mg kg^{-1} TBHQ is sufficient to attain the oxidation stability parameter	[178]
TBHQ	Recycled cooking oil	IP of TBHQ-doped biodiesel raised from 6.8 h to 24 h	EN 14112	After 24 h of the static immersion test, IP of both neat and TBHQ-doped biodiesels decreased below the EN 14214 limit	[179]
PG > BHA > BHT	Mahua oil	The use of antioxidants improved the stability significantly	ASTM D3703-99 for PV & ASTM D445 for kinematic viscosity	The hydroperoxide formation is reduced by the addition of 1000 ppm antioxidant	[180]
PG > TBHQ > BHA	Jatropha oil	The use of PG is preferred for the long-term oxidation stability retention of jatropha biodiesel	EN 14112	By the use of 150 ppm of PG, IP reached 26.35 h after 1 week of storage and is reduced only to 23.59 h by storage for 20 weeks.	[181]
AO2 > AO1 > AO3	Soybean oil	The thermal and oxidative stabilities have been improved	TGA-DTG & Rancimat method	The highest oxidative stability is showed by AO2 by Rancimat method. Thermal analysis results showed AO1 and AO3 as better	[182]
BPH > BHT	Waste cooking oil	The oxidation stability increased with the antioxidant concentration	EN 14112	300 ppm of antioxidants are required to meet EN standard & > 600 ppm antioxidant is required to meet Japanese standard	[125]
δ tocopherol > γ tocopherol > α tocopherol	Sunflower oil, cooking oil, rapeseed oil & tallow	IP increased with antioxidant concentration	IP measurement	Deactivation rate of antioxidant increased with unsaturation in the oil	[183]
PG > PY > TBHQ > BHT > BHA > α-tocopherols	Terminalia oil	Storage stability depends mainly on the antioxidant type and concentration	IP measurement	Stability can be upgraded up to 12 times by 1000 ppm PG	[184]
PY, PG, TBHQ, BHA & BHT	Rapeseed oil, sunflower oil, used frying oil, & beef tallow	BHT was not as effective as other four antioxidants	Rancimat method	Concentrations of antioxidants were varied from 100 to 1000 mg/kg	[185]

AO1 – butylated hydroxyl anisole, AO2 – 2,6-di-tert-butyl-4-methylphenol, AO3 – mixture 2,6-di-tert-butylphenol,+2,4,6-tri-tert-butylphenol, IB – ionol BF 200.

polyethylene and polypropylene, during its contact [43]. Therefore, these plastic materials and Cu-containing tanks are not suitable for the storage of biodiesel. As an alternative to the mentioned materials, Teflon, Viton, fluorinated plastics and nylon are significantly used for biodiesel storage because biodiesel B100 is compatible with these materials to a great extent. In the case of metals and alloys, the compatible ones include aluminium, carbon steel, stainless steel and fibreglass [43]. Storage materials made up of copper, bronze, tin, zinc, etc. may hasten the oxidation of biodiesel and may result in the formation of insoluble sediments. The effect of antioxidants on the stability of metal-contaminated biodiesel samples is discussed below.

Knothe and Dunn investigated the effect of Cu, Fe, and Ni on the biodiesel stability by the IP measurement of methyl oleate at 90 °C, where copper resulted in the smallest IP value compared to the other metal contaminated methyl oleate samples [186]. Jain and Sharma [187] studied the effect of metal contaminants on the stability of biodiesel obtained from jatropha oil with and without antioxidants. Metals such as Fe, Ni, Mn, Co and Cu in different concentrations have been mixed with biodiesel and have been analysed for their storage stability. The concentration of antioxidants that effectively increases the stability of samples containing different metal contaminants is different. In this study, PY is used because it is one of the best antioxidants for stabilising biodiesel without metal contaminants. When mixing 200 g m^{-3} of PY in a sample without metal, the sample acquires an induction period of 6 months. A sample with metals required a greater antioxidant concentration to enhance its applicability. For biodiesel containing approximately 2 g of Fe, 800 g m^{-3} PY is adequate for making the biodiesel stable for at least 5.5 months. However, for other metals, such as Ni, Mn, Co and Cu, the storage time is approximately 3.62, 3.24, 2.76 and 2.07 months, respectively, using 800 g m^{-3} PY.

Sarin et al. [188] investigated the oxidative stability of jatropha-based biodiesel in the presence of metal contaminants. Here, the transition metals in the metal containers, such as Fe, Ni, Mn, Co and Cu were blended as metal naphthenates in different concentrations (ppm) with jatropha-based biodiesel. The oxidative stability of pure biodiesel and metal-contaminated biodiesel with and without antioxidants was considered here. In the absence of metal, the induction period of biodiesel increased from 3.95 h to 6 h with the addition of 200 ppm of BHT. As the metal contaminants were added, the stability decreased and the addition of antioxidants increased the stability. The effect of metals on the stability of biodiesel is catalytic because the IP value of biodiesel becomes constant at some higher concentration and above for all metals. Cu shows the strongest catalytic effect for oxidation, and all other metals also showed catalytic effects on biodiesel oxidation. BHT is the most effective antioxidant in these analyses. However, the concentrations of antioxidants required to meet the EN-14112 specifications of biodiesel depend on the metal.

Yang et al. investigated the oxidation stability of different commercially available biodiesel samples [189]. In their study, Cu

and Pb showed the strongest detrimental effects toward the oxidative stability, and the stability depended on the metal particle size and the oxide coating thickness. The biodiesel samples were quite stable in the presence of aluminium alloy and steel. The influence of the antioxidant PY on the IP of the copper- and the lead-contaminated biodiesel samples was also evaluated. The IP was significantly improved and met the EN-14112 limit with antioxidant addition at the PY concentration in the range 100–200 ppm.

In the study on the effect of antioxidants on the stability of jatropha biodiesel blended with petrodiesel, the amount of antioxidant required to stabilise the blend is less than pure biodiesel. For a blend with biodiesel of less than 20%, no antioxidants are needed. As the amount of diesel is decreased, a small addition of antioxidants is required. Reducing the amount of diesel will also reduce the IP. Approximately 80% of the diesel is required to reach the standard specification of the IP of 20 h for EN 590. Beyond B20, antioxidants are required to acquire oxidative stability. The effect of five antioxidants, namely BHT, TBHQ, BHA, PY and PG, on the stability of biodiesel blends was studied [17,18]. PY is more effective. The optimisation showed that 100 ppm was the optimal concentration of PY for pure *Jatropha curcas* biodiesel, and 50 ppm was required for the B30 blend to maintain the standard specification for the oxidation stability.

10. Emission from antioxidant stabilized biodiesel fuelled engine

There are many studies available on the performance and emission analysis of biodiesel or blended biodiesel fuelled diesel engines [190–194]. But only limited reports are there dealing the performance and emission of antioxidant stabilized biodiesel fuelled engines. The antioxidant showed little (either increase or decrease) influence on the engine performance and fuel properties. Since biodiesel is gaining attention as an eco-friendly fuel, factors affecting its combustion and thus the emission are highly important. Studies on the role of antioxidants in chemical pollution of biodiesel fuelled engines shows that the selection of the antioxidant additive to biodiesel is highly important in determining the pollutant evolution. In the report by Suyin Gan and Hoon Kiat Ng, effect of antioxidant addition to biodiesel on engine emission is investigated in the blends of palm oil biodiesel with diesel (B10 and B20) [95]. It is observed that, among the antioxidants investigated, i.e., BHT, BHA and TBHQ, lowering of NO emission has been displayed by BHA and TBHQ; but their high concentrations in the fuel blends increased the NO levels. Additionally BHA could even decrease the CO emission, but the other two antioxidants failed in this matter. In the investigation by Kivevele et al., it is observed that the addition of 1000 ppm of PY antioxidants to croton oil methyl ester showed negligible influence on the engine exhaust emissions [195]. The emission of CO, NO_x, total hydrocarbons (THCs) and smoke got slightly decreased or increased based on the load applied. The influence of antioxidants BHA, BHT, TBHQ and 2-ethylhexyl nitrate (EHN), in the engine performance and exhaust gas emission of canola oil methyl ester blend (B20) was investigated by Erol Ileri and Gunnur Kocar [97]. It is found that the NO_x emission is decreased upon antioxidant addition in most situations where as CO level got slightly increased. EHN was most effective in decreasing NO_x and TBHQ showed minimal evolution of CO. Jain and Sharma had analysed the emission of jatropha biodiesel fuelled diesel engine and found that the additive, PY has minimal effect on the emission. The exhaust of CO, and THC was slightly decreased, whereas the NO_x formation slightly increased or decreased with engine load [196]. Analysis on the emission of soybean biodiesel fuelled engine shows that the antioxidants are not having any effect on the engine exhaust [197]. According to Varatharajan et al., use of antioxidant additives is one of the most cost-effective ways to lessen the emission of NO_x from biodiesel fuelled engine [198]. But in their study, the formation of CO and THC is increased. The antioxidants selected for the study are EDA, p-PDA, BHT, α-tocopherol and L-ascorbic acid. p-PDA showed the best activity in reducing NO_x emission.

In most of the studies on antioxidant added biodiesel emission analysis, a reduction in NO_x and sometimes a slight increase in CO and THC is observed. Still the amount of CO and THC has been found to be lesser than that emitted by diesel fuel [199]. When compared to the emission from diesel fuel combustion, NO_x formation is the only defect of biodiesel fuel. From the above studies, it is clear that, antioxidants can also play a major role in reducing the NO_x formation [200,201]. The reason for the formation of NO_x is the presence of free radicals in the fuel as already mentioned in this article. The fuel radicals react with nitrogen from the air to form NO_x. The presence of antioxidants can terminate the radical reactions and thus can decrease the NO_x formation.

11. Conclusions

The oxidation stability is one of the major issues for implementing the use of biodiesel as an alternate fuel to petrodiesel. In this review, the various aspects of biodiesel oxidation stability are narrated. The parameters representing the oxidation stability of biodiesel are analysed. Among those parameters, the induction period and the BAPE are the major factors. The important methods available for predicting the biodiesel stability are also reviewed. The analysis of the IR spectra is an effective, fast, easy and non-destructive method. Studies on the effect of antioxidants in improving the oxidation stability reveal that each antioxidants' activity differs based on the type of biodiesel feedstock, the antioxidant concentration, the blending percentage with petrodiesel, storage conditions, etc. Among the different antioxidants, PG is the best antioxidant for most of the biodiesel samples. Antioxidant shows the additional advantage of decrease in the NO_x emission from the biodiesel fuelled diesel engines. Aluminium is the best storage container for biodiesel because it does not have any catalytic effect on biodiesel oxidation.

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